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<p>(21) International Application Number: PCT/NL93/00212</p> <p>(22) International Filing Date: 21 October 1993 (21.10.93)</p> <p>(30) Priority data: 07/966,748 27 October 1992 (27.10.92) US 07/966,747 27 October 1992 (27.10.92) US</p> <p>(60) Parent Application or Grant (63) Related by Continuation US 07/966,748 (CIP) Filed on 27 October 1992 (27.10.92)</p> <p>(71) Applicant (for all designated States except US): DSM N.V. [NL/NL]; Het Overloon 1, NL-6411 TE Heerlen (NL).</p>		<p>(72) Inventors; and (75) Inventors/Applicants (for US only) : LU, Szu-Ping [-/US]; 17136 Birchcrest, Detroit, MI 48221 (US). XIAO, Han, Xiang [CN/US]; 26170 Kiltartan, Farmington Hill, MI 48334 (US). FRISCH, Kurt, Charles [US/US]; 17986 Park Lane, Grosse Ile, MI 48138 (US). WITTE, Francis- cus, Maria [NL/NL]; Albrecht Thaerlaan 70, NL-3571 EH Utrecht (NL). VAN DE PLOEG, Antonius, Francis- cus, Maria, Josephus [NL/IT]; Via Fratelli Bandiera 1, I-Venegono Inf. (IT).</p> <p>(74) Agent: PEELS, Robertus, Elisabeth, Jacobus; Octrooibu- reau DSM, P.O. Box 9, NL-6160 MA Geleen (NL).</p> <p>(81) Designated States: AU, BB, BG, BR, BY, CA, CZ, FI, HU, JP, KP, KR, KZ, LK, MG, MN, MW, NO, NZ, PL, RO, RU, SD, SK, UA, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).</p> <p>Published With international search report.</p>
<p>(54) Title: ACRYLIC BASED POWDER PAINT</p>		
<p>(57) Abstract</p> <p>The invention relates to a powder paint based on acrylics. The thermosetting powder paint comprises a hydroxyl functional acrylic resin and an isocyanate crosslinking agent blocked with a blocking agent wherein the isocyanate crosslinking agent is an adduct of an isocyanate and a mixture of polytetramethylene ether glycol and at least one additional, but other glycol, selected from the group consisting of glycols and polyglycols.</p> <p style="text-align: right;">BEST AVAILABLE COPY</p>		

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ACRYLIC BASED POWDER PAINT

5 The invention relates to a powder paint based on acrylics.

 The mechanical properties of acrylic based powder coatings are worse (pages 162-167 of "Powder Coatings, Chemistry and Technology" by Tosko Misev; John Wiley and Sons, 1991). Acrylic based powder coatings, which are used in practice, are almost exclusively based on epoxy functional acrylic resins cured with long-chain dicarboxylic acids as hardeners. The long aliphatic chain of the crosslinker provides flexibility and impact
15 resistance to the cured film, but still far below the values which are usually obtainable with the other powder coating systems. In most cases the impact resistance of the acrylic powder coatings does not exceed 30 inch-pounds. This is still several times lower compared to the
20 values of polyester and polyurethane based powder coatings.

 It is the object of the invention to provide an acrylic powder coating system which shows excellent hardness, gloss, impact resistance, durability, clearness,
25 chemical resistance and good flexibility.

 The invention is characterized in that the thermosetting powder paint comprises
- a hydroxyl functional acrylic resin and
- an isocyanate crosslinking agent blocked with a blocking
30 agent, wherein the isocyanate crosslinking agent is an adduct of an isocyanate and a mixture of polytetramethylene ether glycol and at least one additional, but other glycol, selected from the group consisting of glycols and polyglycols.

35 Preferably the crosslinker has a melting point higher than 45°C and a molecular weight M_n between 100 and 3000, more preferably between 300 and 1500.

 The mixture of glycols and/or polyglycols

contains preferably more than 50% by weight of polytetramethylene ether glycol as one polyol. More preferably this amount is between 60 and 75% by weight.

Suitable other glycols or polyglycols include a great number of diols, triols and polyols, such as for example butanediol, ethanediol, neopentylglycol, 2,2-bis-(1-hydroxy-2-oxyethylphenyl)propane, 1,1-isopropylidene-bis(phenylene-oxy)di-2-propanol-2, cyclohexyldimethylol, trimethylolpropane, trimethylolethane, adipate polyols, polycaprolactone glycols and polycarbonate glycols.

According to a preferred embodiment of the invention the second additional polyglycol is a polyether polyol. A suitable polyether polyol is Voranol 220-530TM (of Dow).

A suitable polytetramethylene ether glycol is Terathane 1000TM (of Du Pont).

Suitable isocyanates include aliphatic (poly)isocyanates such as for example hydrogenated methylene diphenyldiisocyanate (HMDI), isophorone diisocyanate (IPDI), trimer(isocyanate) of isophorone diisocyanate (T1890TM, Hüls), 1,6-hexamethylene diisocyanate (HDI) and the trimer of 1,6-hexane-diisocyanate (Tolonate HDTTM, Rhone Poulenc), 1,3-bis-(1-isocyanato-1-methylethyl)-benzene (TMXDI; American Cyanamid) or aromatic polyisocyanates, such as for example 2,4 or 2,6-diisocyanatetoluene (TDI) and 4,4'-diisocyanatodiphenylmethane.

Preferably HMDI is used.

The flexible crosslinker can be prepared by first reacting half of the molar equivalents of an isocyanate with the polyglycol mixture and next reacting the remaining isocyanate equivalent with a blocking agent.

A blocked isocyanate is an isocyanate which has been reacted with a material which will prevent its reaction at room temperature with compounds that conventionally react with isocyanates but will permit that reaction to occur at high temperature.

Blocked isocyanates are described by Wicks in

Progress in Organic Coatings (3, 1975, 73-99).

According to a preferred embodiment of the invention the blocking agent is a non-volatile agent having a polymerisable double bond and an oxime function.

5 These agents have the general formula (I):



10

where

$\text{R}^1, \text{R}^2, \text{R}^3 = \text{H}$ or $(\text{C}_1-\text{C}_5)\text{alkyl}$

$\text{R}^4 =$ aliphatic, amide group or organic ester group and

15 $\text{R}^5 = (\text{C}_1-\text{C}_5)\text{alkyl}$.

Preferably the amide group is steric hindered.

The aliphatic group, preferably, contains 1-10 carbon atoms.

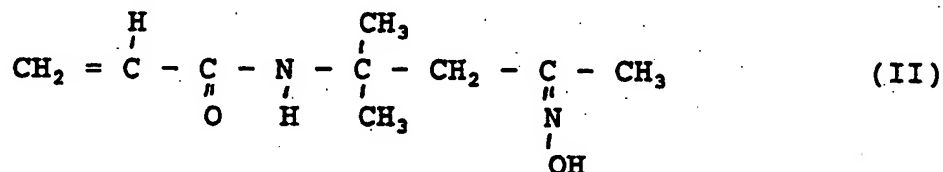
The organic ester group can be characterized by

20

$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{O}-\text{R}^6 \end{array}$ in which $\text{R}^6 = (\text{C}_1-\text{C}_{10})\text{alkyl}$.

The agent having a polymerizable double bond and an oxime function is preferably an acrylamide derivative having the formula (II):

25



30

This suitable blocking agent according to the invention is diacetoneacrylamide oxime (DAAOX). The preparation of DAAOX is disclosed in Macromolecules, Vol. 16, 10, 1983, pages 1561-1563.

35

The use of DAAOX and other blocking agents having a polymerisable double bond and an oxime function is very advantageous, because these blocking agents do not evolve during the cure of a hydroxy-isocyanate powder

paint system. The blocking agent can be polymerized during cure of the powder paint, because they consist of a blocking side and a polymerizable double bond. The polymerizable double bond can be polymerized during the cure of the coating by adding a suitable peroxide. Any peroxide having a suitable half-life-time at the curing temperature of the coatings can be used. Preferably the peroxide has a half-life-time of less than 10 minutes at the temperature at which the coating is cured. The amount of peroxide can vary between 0.5 and 4 wt.%, preferably between 1 and 2%, based on the weight of the added blocked isocyanate crosslinker. Suitable peroxides include tert.-amyl-peroxybenzoate, tert.-butylperoxybenzoate and tert.-butylperoxy-2-ethylhexyl carbonate.

Said non-volatile blocking agents can be obtained from compounds having a ketone or aldehyde group which can be converted into an oxime and having an unsaturated double bond as well. Suitable examples of unsaturated ketones or aldehyde groups include methyl-vinyl-ketone, ethyl-vinyl-ketone, mesityl-oxide, allylacetone, crotonaldehyde, 2-hexanal and citronellal. The blocking agent can be reacted with a (poly)isocyanate in a conventional way. Preferably the molar equivalent ratio (poly)isocyanate: blocking agent is substantially 1:1.

The main features of the isocyanate-hydroxyl curing reaction are described in the foregoing cited Powder Coatings, Chemistry and Technology at pages 56-58.

The use of a non-volatile agent having a polymerizable double bond and an oxime function is not limited to the reaction between a blocked isocyanate and a hydroxyl functional acrylic resin. The hydroxyl functional resin can also be, for example, a polyester or a polyurethane.

Suitable volatile blocking agents include for example phenol, cresol, long-aliphatic-chain substituted phenols such as isononylphenol, amides such as ϵ -caprolactam, active methylene group containing compounds

like malonates such as isopropylidene malonate and acetoacetic esters, sodium bisulfite and oximes such as for example methylethylketone oxime and butanone oxime.

Suitable hydroxyl-functional acrylate resin
5 include for example resins based on hydroxyethyl (meth)acrylate, hydroxypropyl (meth)acrylate and methyl (meth)acrylate. The resin may also be based on methacrylic acid and alkyl esters of (meth)acrylic acid such as methyl acrylate, ethyl (meth)acrylate, isopropyl (meth)acrylate,
10 n-butyl (meth)acrylate, n-propyl (meth)acrylate, isobutyl (meth)acrylate, ethylhexyl acrylate and/or cyclohexyl (meth)acrylate and vinyl compounds such as styrene.

Preferably, the hydroxylacrylate resins have a hydroxyl number between 40 and 150 mg KOH/g resin and an
15 acid number lower than 20 mg KOH/g resin.

The acrylate resins can be prepared by a (co)polymerization, where solvent is fed to a reactor and then heated until the solvent boils. Monomers, and subsequently monomers, initiator and, optionally,
20 mercaptan are added during a period of, for instance, between 2 and 4 hours, after which the temperature is kept at the reflux temperature for, for instance, two hours. The solvent is distilled off by increasing the temperature followed by a vacuum distillation lasting, for instance,
25 one to two hours. Then the product is drained and cooled. Suitable solvents include for example toluene, xylene and butylacetate. Suitable initiators include azo-bis-isobutyronitrile, dibenzoylperoxide and tert.-amyl-peroxy-2-ethyl-hexanoate.

30 The weight ratio polymer:crosslinker is generally between 90:10 and 50:50.

Preferably the molar equivalent ratio of polymer:crosslinker is between 1:0,8 and 1:1,5. Very suitable ratios are between 1:1 and 1:1,2.

35 Obviously, all customary additives may be included in the composition. Examples of customary additives include pigments, fillers, flow aids, stabilizers and catalysts. Suitable pigments include

inorganic pigments, for instance titanium oxide, zinc sulphide, iron oxide and chromium oxide, and organic pigments, for instance azo compounds. Suitable fillers include metal oxides, silicates, carbonates and sulphates.

5 The technology and production of powder coatings is described at pages 224-226 of Powder Coatings, Chemistry and Technology, by Tosko Misev (1991; John Wiley and Sons).

10 Powder coatings according to the present invention can be applied in general industrial and domestic appliances, metal furnitures, architectural applications, automotive topfinishes, corrosion protective coatings and finishes for wood, plastics and paper.

15 US-A-5097010 relates to the preparation of thermally-reversible isocyanate polymer by reacting a labile hydrogen segment with an isocyanate segment. The obtained compositions are useful as hot-melt adhesives, coatings and mouldings and furthermore in injection reaction moulding applications and composite and laminate manufacturing followed by thermal forming and pulltrusion. In contrast to the present invention, it is the object of US-A-5097010 to provide a thermally-reversible system. Furthermore in contrast to the present invention, which relates to thermosetting coatings, said US-patent
25 discloses a thermoplastic system with polymer networks which are insoluble strong solids at room temperature but become soluble free flowing melts at high temperature. Of course the polyurethanes are based on diisocyanates and polyols and a man skilled in the art also knows that long
30 flexible polyols result in flexible polymers. The present invention, however, relates to a flexible network and does not relate only to a flexible resin. It is for a man skilled in the art not obvious that a flexible part in a resin will also result in a flexible network. It is the
35 essential feature of the present invention that the polytetramethylene ether glycol incorporated in a polyurethane resin (together with other diols and diisocyanates) in combination with an acrylate resin results in

a flexible network. Applying polytetramethylen ether glycol as the glycol alone will not result in a superior powder coating resin. The mixture of polytetramethyl ether glycol with at least one other glycol or polyglycol produces the desired properties. One glycol is responsible for the flexibility, the other glycol is responsible for the level of the glass transition temperature.

The coatings of the present invention are further illustrated by the following experiments and examples. The examples are included for illustrative purposes and should not be considered to limit the present invention.

Experiment I

Synthesis of an hydroxyl functional acrylic resin

A 2 L reactor vessel, equipped with a thermometer, a stirrer and a reflux cooler, was charged with 500 g toluene. The reactor was stirred, a nitrogen flow passed through the reactor and the temperature was increased to reflux temperature. A monomer mixture consisting of 417 g methyl methacrylate (MMA), 175 g hydroxyethyl methacrylate (HEMA), 200 g cyclohexylmethacrylate (CHMA), 200 g n-butylacrylate (BA) and 8 g methacrylic acid (MA) was added. In this monomer mixture 29,4 g 2,2-azo-bis-isobutyronitrile (AIBN) was dissolved.

The monomer mixture was fed to the reactor in 2.5 hours. The reflux temperature was maintained in the reactor for another 2.5 hours. Then a separator vessel was included in the setup, and the solvent was removed by a gradual increase of the temperature and application of a vacuum. A clear product was obtained with a glass transition temperature (T_g , Mettler TA-3000, system 5°C/min) of 46°C and a viscosity (η) (measured with Emila rheometer, 165°C) of 350 dPa.s.

Experiment II

Synthesis of diacetone acrylamide oxime (DAAOX)

100 g diacetone acrylamide was dissolved in 375

ml of distilled water and 45.75 g hydroxylamine hydrochloride was added with stirring. A solution of 43.75 g potassium carbonate in 62.5 ml of distilled water was added at room temperature over a period of 20 min. After
5 the addition was completed, most of the oxime product precipitated. The reaction was continued for an additional hour and the precipitate was filtered and washed with 50 ml of ice water twice. The wet crude product was dissolved in ethylacetate (500 ml), the organic layer was separated
10 and crystallized in the refrigerator. The crystallized product was filtered and washed with 100 ml hexane twice. The final product was dried at 40°C in a vacuum oven to yield 77 g of the DAAOX product. The melting point (112°C) of DAAOX was measured by using a DSC.

15

Experiment III

The blocking of IPDI with DAAOX (BIPDI)

40.48 g (10% excess) DAAOX obtained according to Experiment I was dissolved in 50 g methylethyl ketone and
20 22.2 g IPDI was added. The reaction was carried out at room temperature under dry nitrogen. The NCO content was less than 0.1% (by titration) after one hour reaction. The solvent was removed by distillation at 40°C in a vacuum oven overnight. The final blocked IPDI (BIPDI) can be
25 pulverized into fine powder with a melting point of 55-60°C. The blocked NCO content of BIPDI is 13.5% by calculation.

Experiment IV

The blocking of H₁₂MDI with DAAOX (BHMDI)

147.5 g DAAOX (5% excess) obtained according to Experiment I was dissolved in methylethyl ketone (330 g) and 100 g H₁₂MDI was then added. The reaction was carried out at 50°C under dry nitrogen. The NCO content was less
35 than 0.1% (by titration) after one hour of reaction. The solvent was removed at 40°C in a vacuum oven. The final blocked product BHMDI was pulverized to a fine powder and had a melting point (by DSC) of approx. 54°C.

In order to examine the polymerization of BHMDI, the initiator (tert.-amylperbenzoate) was added into BHMDI to initiate polymerization. An exothermic peak was found in the analysis of DSC.

5

Examples I-VII

Preparation of modified crosslinkers

The glycol blend was made by mixing two glycols in a ratio as mentioned in Table I. In a reactor, equipped with a stirrer and under a stream of dry nitrogen the
10 respective glycol blend and the appropriate amount of HMDI (see Table I) were charged. Methyl ethyl ketone (MEK) was added to reduce the viscosity. A small amount of dibutyl-tindilaurate was added (see Table I) as a catalyst, the
15 reaction mixture was heated to 70°C. It was kept at that temperature until the NCO percentage (as determined by titration) was reduced to half of the initial value. DAAOX was dissolved in MEK and then added into the reaction
mixture. The reaction temperature was kept at 70°C until
20 the NCO peak (2270 cm^{-1}) disappeared by checking the infrared spectrum of the product.

After the products in MEK were further diluted with acetone to 25-30% solids content. The dilute
solutions were then added dropwise into cold water under
25 vigorous agitation (> 1500 RPM). The precipitates in the powdered form were then filtered and dried. Glass transition temperature and equivalent weights of NCO are given in Table I.

30 Examples VIII-XIV

Preparation of a powder coating

The powder coating ingredients were weighted (in grammes) in the formulations as showed in Table II. The
formulations were dissolved in acetone to prepare a
35 solution of 25-30% solids content. The solutions were added into cold water dropwise under vigorous agitation. The precipitates in powder form were then filtered and dried. The dried powders were ground into a very fine

particle size. They were sprayed electrostatically on plates and cured as showed in Table II.

The present tests are described at pages 296-303 of Powder Coatings by Misev.

Comparative Example A

0.942 g of BHMDI according to Experiment IV was mixed with 2.058 g acrylic resin according to Example I, and the powder mixture was dissolved in 7.5 g of cellosolve acetate. 0.0015 g dibutyltin diacetate was added as a deblocking catalyst. 0.0188 t-amyl-perbenzoate was added as initiator for the polymerization of DAAOX after deblocking reaction. 0.0585 g of E-25TM was added as flow control agent. The solution of this mixture was coated on steel panels, and the panels were baked at 160°C for 30 min. The coatings were well cured, which was proved by the pencil hardness of 2H and more than 200 acetone rubs. However, the impact resistance (ASTM-D-2794) was less than 30 inchpound.

This shows that the coating made with a non-modified crosslinker has poor properties.

The examples show that the isocyanate crosslinker according to the invention results in very flexible acrylic powder coatings with good properties. The claimed invention results in a remarkable increase in impact resistance.

TABLE I (grammes)

	I	II	III	IV	V	VI	VII
5	HMDI ¹⁾	262	262	20	20	20	20
	Voranol ²⁾	70,0	89,0	-	-	-	-
	CHDM ³⁾	-	-	4,1	-	-	-
	Dianol-22 ⁴⁾	-	-	-	-	-	-
	Dianol-33 ⁵⁾	-	-	6,94	-	-	-
10	1,4-BD ⁶⁾	-	-	-	7,28	-	-
	NPG ⁷⁾	-	-	-	-	2,84	-
	T rat 1000 ⁸⁾	165,0	-	-	-	-	3,20
	T rat 2000 ⁹⁾	-	148,5	9,6	17,0	6,63	7,46
15	DAAOX ¹⁰⁾	193,2	193,2	14,75	14,75	14,75	14,75
	DBTL ¹¹⁾	0,0738	0,0749	0,0135	0,0173	0,0177	0,0118
	MEK ¹²⁾	200	200	50	50	50	50
	Tg (°C) ¹³⁾	56	52	n.m.	n.m.	45	46
	NCO equivalent weight	681	684	749	764	570	586
20	HMDI ¹⁾	= Hydrogenated Methylene Diphenyl Diisocyanate					
	Voranol ²⁾	= Voranol 220-530 (Dow Chemical); polyether polyol					
	CHDM ³⁾	= Cyclohexyldimethanol					
25	Dianol-22 ⁴⁾	= 2,2-bis(1-hydroxy-2-oxy-ethylphenyl)propane					
	Dianol-33 ⁵⁾	= 1,1-isopropylidene-bis(p-phenyleneoxy)-di-2-propanol-2					
	1,4-BD ⁶⁾	= 1,4-butanediol					
	NPG ⁷⁾	= Neopentylglycol					
30	T rat 1000 ⁸⁾	= Terathane 1000 (Du Pont); polytetramethylene ether glycol with molecular weight 1000					
	Terat 2000 ⁹⁾	= Terathane 2000 (Du Pont); polytetramethylene ether glycol with molecular weight 2000					
	DAAOX ¹⁰⁾	= See Experiment II					
	DBTL ¹¹⁾	= Dibutyltin dilaurate					
35	MEK ¹²⁾	= Methyl ethyl ketone					
	Tg (°C) ¹³⁾	= Glass transition point; n.m. = not measured					

TABLE II

	VIII	IX	X	XI	XII	XIII	XIV
5							
R sin Exp. I	100	100	100	100	100	100	100
Crosslinker I	105,3	-	-	-	-	-	-
Crosslinker II	-	105,8	-	-	-	-	-
Crosslinker III	-	-	96,85	-	-	-	-
Crosslinker IV	-	-	-	111,0	-	-	-
Crosslinker V	-	-	-	-	113,1	-	-
Crosslinker VI	-	-	-	-	-	80,61	-
Crosslinker VII	-	-	-	-	-	-	82,82
TI ¹⁾	2,053	2,058	1,968	2,110	2,131	1,806	1,828
TAP ²⁾	1,053	1,058	0,9685	1,110	1,131	0,806	0,828
E ₂₅ ³⁾	2,669	2,075	2,559	2,743	2,770	2,348	2,377
Cur conditions	150°C 30'	150°C 30'	150°C 30'	150°C 30'	150°C 30'	150°C 30'	150°C 30'
Hardness ⁴⁾	> H	> H	2H	> H	> H	> H	> H
Aceton res. ⁵⁾	> 200	> 200	> 200	> 200	> 200	> 200	> 200
Impact res. ⁶⁾	120	110	110	> 160	> 160	> 160	140
- direct	100	60	< 60	> 160	> 160	> 160	120
- reverse							
20							
25							

TI¹⁾ = Dibutyltin diacetate
 TAP²⁾ = Tert. amyl perbenzoate
 E₂₅³⁾ = Flow control agent (DSM)
 Hardness⁴⁾ = Pencil hardness (ASTM-D-3363)
 Ac ton res.⁵⁾ = Acetone resistance (solvent cure test method)
 Impact res.⁶⁾ = Impact resistance (ASTM-D-2794)

CLAIMS

1. A powder paint based on acrylics, characterized in that, the thermosetting powder paint comprises
5 - a hydroxyl functional acrylic resin and
 - an isocyanate crosslinking agent blocked with a blocking agent, wherein the isocyanate crosslinking agent is an adduct of an isocyanate and a mixture of polytetramethylene ether glycol and at least one
10 additional, but other glycol, selected from the group consisting of glycols and polyglycols.
2. Powder paint according to claim 1, characterized in that the additional polyglycol is a polyether polyol.
3. Powder paint according to any one of claims 1-2,
15 characterized in that the blocking agent is an agent having a polymerisable double bond and an oxime-function.
4. Powder paint according to claim 3, characterized in that the agent is diacetone acrylamide oxime.
- 20 5. Use of an adduct of an isocyanate and a mixture of polytetramethylene ether glycol and at least one additional but other glycol selected from the group consisting of glycols and polyglycols as crosslinking agent in the preparation of powder coatings.
- 25 6. A method for preparing a powder paint composition comprising a hydroxyl functional acrylic resin and an isocyanate crosslinking agent which is blocked, characterized in that the isocyanate crosslinking agent comprises an adduct of an isocyanate and a
30 mixture of polytetramethylene ether glycol and at least one additional, but other glycol selected from the group consisting of glycols and polyglycols and the weight ratio of polymer:crosslinking agent is between 90:10 and 50:50.
- 35 7. Method according to claim 6, characterized in that the blocking agent is an agent having a polymerisable double bond and an oxime-function.

8. Method according to claim 7, characterized in that
th agent is diac ton acrylamide oxime.
9. Binder composition comprising a resin and a
crosslinking agent characterized in that the resin is
5 a hydroxyl functional acrylic resin and the
crosslinking agent an isocyanate crosslinking agent
blocked with a blocking agent, wherein the isocyanate
crosslinking agent is an adduct of an isocyanate and
a mixture of polytetramethylene ether glycol and at
10 least one additional, but other glycol, selected from
the group consisting of glycols and polyglycols.
10. Binder composition comprising a hydroxyl group
containing polymer and an isocyanate crosslinking
agent blocked with a blocking agent, characterized in
15 that the blocking agent is an agent having a
polymerizable double bond and an oxime-function.
11. Powder paint composition comprising a hydroxyl group
containing polymer and an isocyanate crosslinking
agent blocked with a blocking agent, characterized in
20 that the blocking agent is an agent having a
polymerizable double bond and an oxime-function.
12. An article coated with a composition according to any
one of claims 1-4 or an article coated with a
composition obtained according to any one of claims
25 6-8.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/NL 93/00212

A. CLASSIFICATION OF SUBJECT MATTER

IPC 5 C08G18/12 C08G18/28 C08G18/62 C08G18/66 C08G18/40
C08G18/48 C08G18/67 C08G18/81 C09D5/03 C09D175/16

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 5 C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	FR,A,2 568 884 (STEVENS-GENIN) 14 February 1986 see claims 1-3 see page 1, line 1 - line 4 see page 4, line 16 - line 27 ---	1
A	EP,A,0 327 031 (ASAHI KASEI) 9 August 1989 see claims 1,7,9 -----	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Information on patent family members

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